REARRANGEMENT OF ALKYL AMINES
PREPARATION OF NITRO AND
AMINO PROPYL BENZENES

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

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ENTITLED Rearrangement of Alkyl Amines - Preparation of Nitro and Amino Propyl Benzenes

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY.

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REARRANGEMENT OF ALKYL AMINES

INTRODUCTION.

In 1871 A. W. Hofman heated aniline hydrochloride and methyl alcohol in a closed tube at a high temperature and succeeded in obtaining monomethyl aniline, dimethyl aniline and other amines with the methyl group in the benzene nucleus. This experiment was an interesting one but many questions which might be asked concerning it were left unanswered by Hofman. Among some of these questions the following may be mentioned: Is this reaction an inter or intra-molecular one? Are there any side-products of the reaction and, if so, what are they? At what stage of the operation does the rearrangement take place? Will a similar rearrangement take place with propyl alcohol?

The whole problem is one which will take years of work to solve as it involves the study of the rearrangement itself, the working out of a method for the quantitative separation of the various primary, secondary and tertiary amines which are formed; a study of all the possible compounds resulting from such a rearrangement; and, if the benzene sulphonyl chloride method of separation proves to be successful, the preparation of the benzene sulphonyl derivatives of each of these amines and their characterization.

The problem is also interesting from a commercial standpoint as this reaction is already being put to good use in the dye industry.

HISTORICAL.

In 1871 A. W. Hofman (1) succeeded in obtaining dimethyl and monomethyl aniline and in addition thereto the replacement of every hydrogen in the benzene ring save one with the methyl group by simply heating aniline hydrochloride with methyl alcohol in a closed tube at a high temperature. His method was as follows:

Ten kilograms of crystallized aniline hydrochloride were heated for 8-10 hours with six kilograms of methyl alcohol at a temperature of 280°- 300°. Strong sodium hydroxide was then added to the product and the basic oil was distilled off with steam. The final product gave no tests for aniline but did appear to contain methyl and dimethyl aniline and higher boiling products. These amines were all changed over into the hydrochloride again and heated anew with excess of methyl alcohol for 12 hours at 300°. Attempts were made to separate the product into its components by fractionation but without success. The presence of dimethyl aniline, dimethyl toluidine, dimethyl xylidine and dimethyl cumidine was proven by treatment of the different fractions with methyl iodide, thus forming the quaternary compound; the corresponding chloride was obtained by use of silver chloride, and finally the platinum salts were formed. Analyses were made of the platinum salts, also of the iodine compound, and in some cases determinations of carbon, hydrogen and nitrogen were run. All of these analyses gave results which checked with the theoretical values of the compounds mentioned above. Hofman believed that in this reaction the nitrogen was first methylated and than then the benzene ring was attacked, the methyl group taking the place of the various hydrogen atoms by shifting from the nitrogen to the ring

carbon atoms. He says that there is no doubt but that methyl chloride is formed and that it is the active agent in the reaction.

In 1872 Hofman (2) found that the quaternary compound, trimethylphenyl ammonium iodide, can exist for a long time at a temperature of 200° without decomposition but, if heated to 220°-230° for 24 hours, a change is noticeable; and when the temperature is raised to 325° (boiling point of lead), the decomposition is complete. These changes are characterized by physical differences in the products.

In Hofman's experiments one mole of methyl iodide was added to one mole of pure dimethyl aniline in a hard glass tube and the mixture was heated to 220°- 230°. The products were dimethyl toluidine and small quantities of methyl and dimethyl xylidine. The existence of these compounds were proven as before by the analyses of their platinum salts.

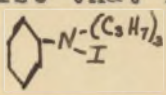
A similar mixture was heated to 325°. Qualitative tests proved the presence of a primary amine and fractionation and analyses showed the primary amine to be cumidine.

In another article (3) Hofman states that it is possible to go from methyl aniline over into toluidine by a similar method.

In 1874 Hofman (4) stated that when aniline hydrochloride is heated with ethyl alcohol or amyl alcohol, the ethyl or amyl group will rearrange into the benzene ring. However, no rearrangement of phenyl group into the ring takes place when phenyl aniline hydrochloride is heated nor does rearrangement occur in the aliphatic series.

THEORETICAL

Derick and Bornmann (5) showed that diacyl amines will rearrange when heated, the change being from a compound of high ionization constant to a compound with a lower constant.

It was hoped to show that a similar rearrangement to that performed by Hofman occurs with propyl alcohol and also that it does not take place until the quaternary compound  is formed. One reason for this theory is that the ionization constant of the quaternary compound is considerably higher than those of the rearranged products and hence the tendency would be towards rearrangement, viz., the going over from a less stable compound to a more stable one, the ionization constant being a criterion of stability (6). Moreover, the ionization constants of the primary, secondary and tertiary amines differ but slightly from those of the rearranged products, and therefore they will be comparatively stable.

EXPERIMENTAL.

Introduction.

Since the accomplishment of this investigation necessitates a careful quantitative study of the preparation of aminopropylbenzenes by the Hofman reaction, an accurate quantitative method for the determination and the separation of the products is absolutely essential. The method chosen was that of the formation of the benzene sulphonyl derivatives (7). But no literature exists concerning the properties of the benzene sulphonyl derivatives of propylamino- or aminopropylbenzenes.

The first step in this investigation was the preparation of such derivatives from the amines. It seemed best to make the ortho and para-aminopropylbenzenes from the corresponding nitropropylbenzenes since the latter could be prepared by the direct nitration of propylbenzene. Propylbenzene could easily be obtained by the Fittig synthesis from brombenzene and propyl bromide.

Propylbenzene.

General

There are two general methods for introducing an alkyl group into the benzene ring, viz., the Friedel-Craft's reaction and Fittig's synthesis.

The theory of the Friedel-Craft's reaction is still in dispute. One explanation is that the aluminium chloride forms the compound $C_6H_5AlCl_2$ with benzene and that this reacts with the alkyl halide, aluminium chloride being regenerated, the alkyl group going into the ring and copious quantities of hydrochloric acid being formed. The yields are frequently unsatisfactory. Better yields are obtained with homologues of benzene than with benzene itself. Poor yields are obtained very often due to the fact that the action of the aluminium chloride on undiluted substances is too violent and leads to the formation of resins. Carbon disulphide or chloroform is therefore used to dilute the substances; they insure quicker action, keep the temperature at 50°, which appears to be favorable, and they also moderate the violent action of water on the products and prevent the formation of resins.

The above method is not as satisfactory as the Fittig synthesis in which the alkyl group is substituted for the halogen in the benzene ring by the use of sodium. Comparing the Fittig

synthesis with the Friedel-Craft's reaction, the former is less violent if it is not heated; there is less chance of rearrangement, but there is more danger due to the sodium. The sodium is either used in the form of thin slices or as sodium wire. Gattermann (8) gives the yield as 61% of the theoretical.

Propylbromide. $CH_3CH_2CH_2Br$ (B.p. 70.82°)

This was made by pouring 100 g. of phosphorus tribromide in small portions thru a reflux condenser upon 82 cc. of propyl alcohol and heating the mixture for one hour on a water bath. The reaction proceeded vigorously. The product, a heavy yellow liquid, was washed with water, dried over calcium chloride and then fractionated by heating over a water bath. This method was later modified by reversing the operation, viz., pouring the propyl alcohol in small portions upon the phosphorus tribromide as this was found to reduce the violence of the reaction. It was also learned that safety to the experimenter was only insured when the flask was shaken after each addition in order to thoroughly mix the two layers. The percentage yields were 41%, 39.3%, 45.9% and 45.9%.

Another method consisted in taking propyl alcohol (9) and hydrobromic acid (Sp. G. 1.49) and gently heating them under a reflux condenser for a period of three to four hours. The proportions used were as follows: one part by weight of alcohol to approximately five parts of the acid. The propyl bromide separated out as a yellow liquid, forming the upper layer in the flask. This was distilled off from the dilute hydrobromic acid, dried over calcium chloride, and the resulting product was fractionated. This method was fairly satisfactory but great care had to be taken to prevent loss from evaporation or imperfect condensation. Yields: 35%, 41%

50% and 43%. The dilute hydrobromic acid was added to strong hydrobromic acid (Sp. G. 1.49) and the resulting mixture was used in treating more propyl alcohol.

Still another method is represented by the equation

$$3C_3H_7OH + 3Br + P = 3C_3H_7Br + P(OH)_3$$

Ten grams of red phosphorus and 80 g. of propyl alcohol were put in a 150 cc. distilling flask and 90 g. of bromine were allowed to drop in slowly (10). The mixture was shaken from time to time and the propyl bromide was distilled off by heating over a water bath. The distillate was treated with a dilute solution of sodium hydroxide to free it from bromine; washed with water several times; dried over calcium chloride; filtered and distilled. Yields, 54%, 35% and 45.2%.

Propyl iodide. $CH_3CH_2CH_2I$ (B.p. 102.2°).

This method is similar to the one given in the preceding paragraph for propyl bromide. The proportions used were those recommended by Noyes (11) in a similar experiment. Fifty-four grams of propyl alcohol were added to 9 g. of red phosphorus in a distilling bulb and 75 g. of iodine were then added in small portions. Contrary to expectations the reaction proceeded very slowly and instead of having to cool down the temperature, it was necessary to apply heat. This may have been due to the presence of the propyl group. The resulting propyl iodide was distilled off, washed with water and sodium hydroxide to free it from iodine, dried over calcium chloride and redistilled. The product was 59 g. of propyl iodide, boiling between 101° and 102°. Yield, 23%.

Propylbenzene by the Friedel-Craft's Reaction. $C_6H_5CH_2CH_2CH_3$

$$C_6H_6 + AlCl_3 + C_3H_7Br = C_6H_5C_3H_7 + AlCl_3 + HBr$$

Fifty-six grams of propyl bromide and 15 g. of benzene were placed in a flask with a reflux condenser. Aluminium chloride was added in small portions thru the condenser until 5-6 grams had been used. The flask was shaken after each addition but even then it was three or four minutes before the reaction began. A large amount of hydrobromic acid and hydrochloric acid escaped thru the top of the condenser. Toward the end of the reaction heat was applied and two layers formed, theupper layer being yellow and the lower red. The contents of the flask were poured into water whereupon decomposition took place. The upper brownish-yellow layer was separated from the rest of the liquid, dried over calcium chloride, filtered thru a filter paper wet with benzene, and then fractionated. After two fractionations it was evident that the propylbenzene obtained was going to be such a small quantity that it was not worth while to go further. It was found later than an error had been made in calculating the proportions. According to Gustavson (12) the proportion should be 3 parts by volume of benzene to 2 parts of the alkyl halide. Another reason for the poor yield was that no carbon disulphide or chloroform had been used to slow up the reaction. This method of synthesis was now abandoned and that of Fittig tried.

Propylbenzene by the Fittig synthesis. $C_6H_5CH_2CH_2CH_3$ (B.p. 157°)

$$C_6H_5Br + C_3H_7Br + 2Na = C_6H_5C_3H_7 + 2NaBr$$

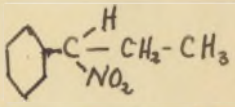
Quantities used: 27 g. of sodium; 100 cc. of ether; 60g. of brombenzene; 55 g. of propyl bromide. The ether was allowed to stand over sodium for several days and was thus obtained free from

water and alcohol. All the sodium used was run thru the sodium press. The sodium and ether were placed in a 500 cc. round bottom flask and a long reflux condenser used. The brombenzene and propyl bromide were added thru the reflux condenser. The reaction begins in a short time. The temperature of the mixture rises to its boiling point and a steady stream of condensed vapor falls back into the flask. This continues for several hours when it ceases. Usually the flask is allowed to remain untouched for at least 24 hours. By that time there is no liquid visible but instead a bluish mass --in part a powder. The flask is placed over a water bath for several hours to drive off the ether and then heated directly by a luminous flame, using an air condenser (the boiling point of propyl benzene is 157°). The distillate is a yellow liquid which has to be fractionated. Variations in the time of reaction were made but no appreciable difference in yields was noticed. Larger quantities of materials were also used but the reaction proved to be too violent and considerable loss was experienced each time due to difficulty in controlling the experiment. Yields, 52.4%, 34.7%, 38.3%, 58%, 60% and 55%.

Nitropropylbenzene.

General.

In looking up the literature for nitropropylbenzene it was a matter of considerable surprise to discover that this comparatively simple compound had never been prepared.

Konowalow (15) made ∝nitropropylbenzene  by mixing 4 cc. of propylbenzene with 25 cc. of nitric acid (Sp. G. 1.075) and keeping the mixture at a temperature of 105° - 108° for 7 hours. Its boiling point is 141° under 25 mm. pressure. Under

atmospheric pressure it boils at 245° - 246° with partial decomposition.

Nitroethylbenzene has been made by Beilstein and Kühlberg (14) and there was no reason to doubt that nitropropylbenzene could be prepared similarly.

Method.

Equal volumes of fuming nitric acid (Sp. G. 1.516) and propylbenzene were used, this being four times the theoretical amount of the acid required. The acid was added in small portions to the propylbenzene and the temperature kept down by immersing the flask in an ice bath. Brown fumes were given off and intense heat was generated. The end of the reaction was denoted by the cessation of the crackling noise when the acid was added. The final product was a cherry-red liquid. This was poured into water and formed red globules on the bottom of the beaker. An aqueous solution of sodium carbonate was added until it was alkaline (pretty hard to tell) and this changed the red globules into a yellow emulsion which rolled up into balls upon shaking. The emulsion was extracted with ether, the ether driven off and the nitropropylbenzene dried over calcium chloride. In order to obtain the largest possible yield of nitropropylbenzene, "salting out" was resorted to and the calcium chloride was also extracted with ether.

Separation of ortho and para-nitropropylbenzene.

An attempt was made to distill the product under atmospheric pressure but decomposition took place and a considerable quantity was lost by being charred in the flask. The only feasible method was distillation under reduced pressure and fractionation after fractionation was made in order to obtain a pure product. It was not until 161 grams of crude nitropropylbenzene had been pre-

pared and fractionated that any results at all were obtained.

The main object in distilling under reduced pressure is the absolute control of all conditions, viz., temperature, pressure, rate of distillation, etc. In order to insure even heating a Wood's metal bath was used, the flame being protected from atmospheric disturbances by a tile. Even then it was found that the gas pressure varied enough to make absolute control very difficult. A Claisen distilling bulb was used and a small stream of air admitted to prevent bumping. Two kinds of receivers were tried, viz., Raikow's and Bruhl's. The latter proved to be more satisfactory. A manometer and a pressure flask to protect the manometer made up the apparatus.

The distillate was a pale yellow liquid which deepened in color upon standing in the light. It was kept in the dark as much as possible to prevent decomposition.

The results of the fractional distillation are shown in Tables A, B, C, D and E.

Properties of ortho-nitropropylbenzene.

Fraction 2(b) was selected as representative of the ortho-compound and its boiling point was determined by Siwoloboff's method (15). The results obtained were not very satisfactory. Although the test tube was not immersed in the bath until the temperature was above the boiling point of the nitropropylbenzene, nevertheless it showed signs of partial decomposition before a reading could be taken and by the time a second reading was secured the color was very dark indeed. It was very seldom that more than two readings were secured on a given sample. The following results (uncorrected) were obtained: 242°, 240°- 241°,

242.6° (first readings); 242.5°, (second reading); 240°-241°, 240°-241° (third readings).

Once more considering fraction 2(b) as representative of the ortho compound, its index of refraction was determined by an Abbé refractometer, using white light and correcting for dispersion. An average reading of $(N)^{22.4°} = 1.5316$ was obtained by approaching it from both sides and changing the dispersion after each reading. The average reading for dispersion was 32.1. The index of refraction and dispersion of the other fractions were obtained in a similar manner. (See Table F.)

The amount of nitrogen in fraction 2(b) was ascertained by the Dumas method.

Theoretical.	Experimental.
8.48%	8.91%

Properties of para-nitropropylbenzene.

Fractions 2(d) and 3(d) were selected as representative of the para compound. By Siwoloboff's method the following boiling points were obtained:

For 2(d) -- 250.2°, 252.3° (first readings); 250.3°, 251.4° (second readings).

For 3(d) -- 251.8° (first reading); 251.3°, 251.9° (second readings).

The same difficulties in determining the boiling point were met here as were experienced with the ortho compound.

The indices of refraction of these two fractions (as given by the Abbé refractometer at 22.7°) were 1.5365 and 1.5370 respectively, while the dispersion readings were 30.6 and 30.8.

The specific gravity of para-nitropropylbenzene was found to be 1.1018 at 26.5°. This was determined with a Westphal balance.

The Dumas method for nitrogen gave the following results:

Theoretical.	Experimental.
8.48%	8.90%

CONCLUSIONS.

It is a general rule in chemistry that a group will enter the benzene ring ortho and para to a methyl, ethyl or propyl group; also that the ortho compound is the lower boiling of the two substances. It is upon these general laws that our conclusions in regard to the nature of the products of the nitration of propylbenzene are based.

Upon examination of Table A it will be seen that there was a sharp break in the distillation between fractions 4 and 5 and it may therefore be concluded that fraction 5 is para-nitropropylbenzene while the other fractions are mainly ortho-nitropropylbenzene. This view is confirmed by the boiling point of fraction 5 when it was refractionated and also by its index of refraction and dispersion reading.

Although it cannot be stated positively that the products obtained were ortho- and para-nitropropylbenzene since time did not permit the preparation of the ortho- and para-propylphenol through the diazonium reaction (these compounds being known) (16) (17), yet it seems safe to say, relying upon the general rule stated above and also upon experimental data, that ortho- and para-nitropropylbenzene were obtained in a fairly pure state.

From the indices of refraction, the dispersion readings, and the boiling points it was concluded that fractions 3(a), 4(a), 1(b), 2(b), and 1(c) were ortho-nitropropylbenzene; that 3(b) and 2(c) were a mixture of the ortho and para compound; that 4(b), 5(b), 3(c), 4(c), 2(d), 3(d), 4(d) and 5(d) were para-nitropropylbenzene.

The boiling point of ortho-nitropropylbenzene lies between 240°-242.6° under a pressure of 745.5 mm.

The boiling point of para-nitropropylbenzene lies between 250.2°- 252.3° under a pressure of 739.8 mm.

The index of refraction of ortho-nitropropylbenzene lies between 1.5310 and 1.5330 at 22.5°.

The index of refraction of para-nitropropylbenzene lies between 1.5360 and 1.5380 at 22.5°.

The dispersion reading for ortho-nitropropylbenzene lies between 31.8 and 32.5.

The dispersion reading for para-nitropropylbenzene lies between 30.5 and 31.1.

The specific gravity of para-nitropropylbenzene is 1.1018 at 26.5°.

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Table A.

First Fractional Distillation.

Time	Fraction No.	Yield	Pressure	Outside Temp.	Inside Temp.	Remarks.
10:16			19 mm.	143.0°	131.0°	First drop came over
10:18			"	143.0°	132.0°	Rate-8 drops in 30 sec.
10:20			"	143.7°	133.3°	" 11 " " " "
10:24	1	14cc	"	143.8°	134.0°	Yellow distillate.
10:25			"	143.9°	134.3°	
10:31			"	145.0°	135.2°	
10:34			"	145.2°	135.7°	Rate-7 drops in 30 sec.
10:39			"	147.0°	137.0°	
10:41			"	148.2°	137.3°	" 22 " " " "
10:43			"	148.0°	137.5°	Yellow distillate
10:45	2	29 cc	"	148.0°	137.3°	
10:47			"	149.0°	137.8°	Losing some of dist. as
10:53			"	149.1°	138.5°	it does not condense.
10:56			"	149.4°	139.0°	Rate-21 drops in 30 sec
10:58			"	150.1°	139.5°	
10:59			"	150.0°	139.5°	
11:01			"	150.6°	139.5°	
11:04			"	150.9°	139.6°	
11:06	3	16 cc	"	150.9°	140.2°	Rate-14 drops in 30 sec
11:09			"	151.3°	140.6°	
11:11			"	151.8°	141.2°	
11:13			"	151.9°	141.3°	
11:16			"	152.6°	142.0°	
11:17			"	152.7°	141.9°	Rate-6 drops in 30 sec.
11:23			"	152.0°	141.8°	
11:25	4	5 cc	"	152.7°	141.5°	" 3 " " " "
11:29			"	152.6°	141.3°	Only 5 cc. distilled in 12 minutes. SHARP BREAK. Turned up flame.
11:32			"	157.0°	144.0°	Rate-33 drops in 30 sec.
11:34			"	159.8°	145.8°	
11:35			"	161.0°	146.5°	Rapid distillation.
11:36			"	161.2°	147.8°	
11:37			"	162.3°	149.3°	
11:39	5	22 cc	"	163.8°	149.9°	Rate-25 drops in 30 sec
11:42			"	166.1°	151.2°	
11:44			"	168.0°	152.1°	Evidently this fraction
11:46			"	171.0°	153.0°	is para.
11:48			"	174.0°	153.8°	
11:51			"	175.0°	155.4°	

Table B

Redistillation of Fraction No. 1.

Time	Fraction No.	Yield	Pressure	Outside Temp.	Inside Temp.	Remarks.
11:21			15.5 mm	140.0°	119.5°	First drop came over
11:23	1(a)	3 cc	15.0 "	141.0°	123.0°	
11:24			"	141.8°	125.5°	
11:25			"	142.0°	126.7°	
11:26	2(a)	3 "	"	143.0°	127.7°	Moderate rate of
11:28			"	143.0°	128.0°	distillation
11:29			"	143.5°	129.7°	
11:30	3(a)	3.5 "	"	143.2°	130.6°	Rate-16 drops in 30 sec
11:32			"	142.4°	131.2°	
11:35			"	146.5°	131.0°	
11:36			"	146.2°	131.2°	Fluctuating.
11:38	4(a)	1 "	"	150.0°	131.8°	Slow distillation.
11:40			"	152.0°	131.5°	
11:43			"	153.0°	131.2°	Sank once to 127°
						Only 3-4 cc. left in flask.
						Turned up flame.
11:45	5(a)	2 "	"	178.0°	140.0°	
						Residue of 1-2 cc. left in flask.

Table C.

Redistillation of Fraction No. 2.

Time	Fraction No.	Yield	Pressure	Outside Temp.	Inside Temp.	Remarks.
10:59			20.0 mm	157.0°	129.0°	First drop came over
11:00			19.0 "	156.0°	131.1°	
11:02			"	155.5°	131.5°	Slow distillation.
11:04			"	156.0°	131.3°	Fluctuating.
11:07			"	154.3°	130.7°	
11:09			"	154.0°	129.8°	Rate-6 drops in 30 sec
11:12	1(b)	9 cc	"	155.0°	130.3°	
11:15			"	155.0°	129.2°	Fluctuating.
11:17			"	152.0°	128.5°	
11:19			17.5 "	153.0°	123.5°	
11:23			"	154.0°	127.7°	
11:26			"	153.0°	128.2°	
11:30			"	154.0°	128.5°	Fluctuating over a
11:33			"	154.5°	129.2°	range of 3 degrees.
11:38			"	158.0°	131.6°	
						Went away; in afternoon found that back pressure had caused water to flow thru apparatus.
9:40			18.0 "	157.8°	129.5°	
9:42			"	156.5°	134.3°	Rate-25 drops in 30
9:43			"	155.0°	133.9°	seconds.
9:44	2(b)	10 "	"	154.0°	133.5°	Distillation is slower
9:46			"	155.0°	134.1°	
9:48			"	155.8°	135.1°	
9:50			"	157.1°	135.7°	
9:53			"	161.0°	137.1°	Rate of distillation
9:54	3(b)	5 "	"	161.4°	138.2°	increases.
9:55			"	164.0°	140.3°	
9:56			"	164.5°	142.3°	
9:57	4(b)	2 "	"	165.0°	142.0°	Fluctuating.
9:58			"	167.0°	143.0°	
9:59	5(b)	1.5 "	"	169.8°	145.0°	
						Inside temp. sank below 130° while outside temp. was above 170°. Nevertheless no distillation; evidently some higher boiling compound present.

Table D.

Redistillation of Fraction No. 3.

Time	Fraction No.	Yield	Pressure	Outside Temp.	Inside Temp.	Remarks.
9:13			17 mm.	165.6°	125.5°	
9:14			"	166.2°	132.2°	Distilling rapidly.
9:15	1(c)	4 cc.	"	165.6°	132.1°	Considerable bumping.
9:17			"	166.7°	134.0°	Rate-19 drops in 30 sec
9:18			"	167.8°	135.2°	
9:19			"	167.0°	135.5°	
9:20	2(c)	3 "	"	166.2°	136.1°	
9:21			"	167.0°	136.4°	Temperature almost
9:22				166.2°	137.0°	constant.
9:23			"	167.1°	138.0°	Rate-18 drops in 30 sec
9:24	3(c)	2 "	"	167.2°	139.5°	Fluctuating.
9:26			"		132.0°	
			"		131.5°	
9:27			"	165.6°	130.2°	Practically stopped
			"		134.0°	distilling over.
9:28			"		129.5°	
	4(c)	2.5 "	"		127.5°	
			"	170.5°	135.0°	Turned up flame.
9:29			"	181.0°	139.0°	
9:30			"	186.5°	142.5°	Fairly rapid distilla-
9:31			"	192.0°	145.8°	tion.
9:32			"	198.0°	145.5°	
						Left in flask- 0.5 cc.

Table E
Redistillation of Fraction No. 5

Time	Fraction No.	Yield	Pressure	Outside Temp.	Inside Temp.	Remarks.
9:59			15 mm.	156.0°		Thermometer thread not
10:00			"	163.0°	130.5°	in sight; bumping;
10:01	1(d)	4 cc	"	164.0°	133.5°	admitted more air;
10:02			"	165.0°	131.5°	Couple cc. carried over mechanically.
10:07			16 mm.	164.0°	137.5°	
10:09			"	162.0°	137.8°	Rate-21 drops in 30
10:11			"	163.5°	137.8°	seconds.
10:12	2(d)	6 "	"	163.0°	138.1°	Rate-19 drops in 30
10:13			"	160.5°	138.2°	seconds.
10:15			"	160.3°	137.4°	
10:16			"	162.0°	137.8°	
			"	162.4°	138.6°	
10:17			"	162.9°	139.2°	
10:19			"	161.0°	138.6°	
10:20			"	162.0°	138.7°	Slow distillation.
10:23			"	163.0°	139.2°	Rate-5 drops per 30
10:24	3(d)	4 "	"	164.0°	139.7°	seconds.
10:26			"	159.0°	139.6°	
10:28			"	161.3°	139.4°	
10:31			"	160.9°	136.2°	Hardly any distilla-
10:32			"	162.0°	140.2°	tion.
10:33			"	160.3°	140.4°	
10:34			"	160.1°	139.8°	Rate-2 drops in 30 sec
10:35			"	161.8°	140.3°	
10:36			"	162.3°	141.0°	
10:38	4(d)	3 "	"	162.2°	141.8°	
10:39			"	159.8°	141.5°	
10:40			"	161.0°	141.3°	
10:41			"	162.3°	142.1°	
10:42			"	162.3°	142.3°	Rate of distillation
10:43			"	162.0°	142.7°	increases.
10:45			"	160.2°	137.6°	Rate-7 drops in 30 sec
10:47			"	158.9°	138.3°	
10:48			"	160.0°	127.0°	Temperature falling.
10:49			"	162.3°	141.0°	
10:57	5(d)	4 "	"	161.0°	138.0°	
10:59			"	163.0°	142.8°	
11:02			"	167.9°	145.0°	Turned up flame.
11:04			"	176.1°	147.2°	
11:06			"	179.0°	140.5°	Turned up flame again
11:07			"	184.0°	147.9°	
11:08			"	189.0°	149.4°	
11:09			"	195.0°	157.0°	
11:10			"	198.0°	159.4°	

Fraction	Inside Temp.	Pressure	Dispersion	Yield	Refractive Index	Frac
1	131.0°-135.7°	19 mm.	31.8	14 cc	1.5304 at 24.5°	1(2(3(4(5(
2	137.0°-139.5°	"	31.6	29 "	1.5313 at 25.0°	1(2(3(4(5(
3	139.5°-142.0°	"	31.4	16 "	1.5329 at 25.3°	1(2(3(4(
4	141.9°-141.3°	"	31.4	5 "	1.5340 at 25.3°	
5	144.0°-155.4°	"	30.7	22 "	1.5363 at 25.1°	1(2(3(4(5(

lde Temp.	Pressure	Dispersion	Yield	Refractive Index	Siwoloboff's Method
.0°-125.5°	15 mm.		3 cc		
.7°-128.0°	"		3 "		
.7°-131.0°	"	32.3	3.5 "	1.5340 at 17.8°	
.2°-131.2°	"	32.3	1 "	1.5350 at 18.3°	
.40°	"		2 "		
.6°-131.6°	17-19 mm	32.5	9 "	1.5310 at 22.4°	
.5°-135.7°	18 mm.	32.1	10 "	1.5316 at 22.4°	240°-242.6°
.1°-140.3°	"	31.6	5 "	1.5347 at 22.4°	
.5°-142.0°	"	31.1	2 "	1.5362 at 22.0°	
.0°-145.0°	"	30.5	1.5 "	1.5369 at 22.1°	
.5°-134.0°	17 mm.	31.8	4 "	1.5324 at 22.1°	
.2°-137.0°	"	31.7	3 "	1.5342 at 22.5°	
.0°-139.5°	"	30.9	2 "	1.5360 at 22.5°	
.0°-145.5°	"	30.7	2.5 "	1.5379 at 21.7°	
0°-131.5°	15 mm.	30.9	4 "	1.5363 at 22.7°	
5°-138.6°	16 "	30.6	6 "	1.5365 at 22.7°	250.2°-252.3°
2°-140.2°	"	30.8	4 "	1.5370 at 22.8°	251.3°-251.9°
3°-142.1°	"	30.6	3 "	1.5370 at 22.6°	
3°-159.4°	"	30.7	4 "	1.5376 at 22.5°	

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